

Resolving Apparent Contradictions in Equilibrium Measurements for Clathrate Hydrates in Porous Media

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A conceptual model for hydrate equilibrium in media with broad pore-size distributions is used to interpret methane hydrate equilibrium experiments in silica gel pores with nominal radii of 2, 5, and 7.5 nm. While the hydrate equilibrium pressure is an intensive property, it is demonstrated that the presence of a broad pore-size distribution in a porous medium causes the experimental pressures to appear extensive. It is observed that the sample size, the headspace volume, the temperature at which the experiments are started, and the amount of hydrate allowed to dissociate to establish equilibrium at this initial temperature all affect the observed pressure at any given temperature. The pore-volume distribution of the porous medium (not the nominal pore radius) and the percent conversion of pore-water to hydrate also affect the measured equilibrium pressures. As a result, measured equilibrium pressures at a specific temperature for identical media can be significantly different, while those for different media may be superposed. These seeming inconsistencies, their causes, and interpretations are examined and explained. Apparently fundamental problems in experimental data are removed when the number of degrees of freedom is properly included in the interpretation.

Introduction

Gas hydrates, formed from light hydrocarbons and water at high pressures and ordinary temperatures, result in crystalline, ice-like clathrates in which the gas molecules are occluded. Their study in porous media is relevant to hydrate formation in gas reservoirs. Studies by Makogen¹ in sandstones with nominal pore radii of 5.7, 5.0, and 3.5 μm suggested that the equilibrium pressure increased as the pore size decreased, but for large pores was nearly identical to that in the bulk.² Handa and Stupin³ studied methane and propane hydrates in silica gel with nominal 7.5 nm pores, and Uchida et al.⁴ investigated the properties of methane hydrate in three Vycor samples with nominal pore radii of 25, 15, and 5 nm. In a recent work⁵ the authors presented measurements for propane hydrate formation in silica gels with nominal pore radii of 7.5, 5.0, 3.0, and 2.0 nm.

Henry et al.⁶ and Clarke et al.⁷ proposed interpretations of the data of Handa and Stupin³ using a modified van der Waals and Platteeuw⁸ equation. The authors of these interpretations^{6,7} suggested that the failure of the models may have been due to the broad pore-size distribution⁹ present in the porous media. In line with these suggestions, we conjecture that gas hydrate equilibrium pressures in porous media with broad pore-size distributions would depend on the ratio of the headspace volume (the volume of the free space exterior to the porous medium and interior to the reaction chamber) to the amount of hydrate present in the sample. The latter depends on the amount of silica gel used, the amount of sorbed water, the percent conversion of this water to hydrate, and the amount of hydrate allowed to

dissociate prior to the first pressure–temperature equilibrium measurement. (See Experimental Methods section below.) Also affecting the observed equilibrium pressures would be the temperature at which the first pressure–temperature equilibrium measurement is made, and the pore-volume distribution of the medium. These considerations imply that, due to the effect of the pore-size distribution, the equilibrium pressures measured in porous media involving broad pore-size distributions appear to be extensive, even though they are not. This work presents experimental evidence supporting these assertions, demonstrates how differences in sample preparation can result in apparent discrepancies in observed hydrate equilibrium pressures for porous media involving broad pore-size distributions, and shows how these apparent discrepancies in experimental data can be reconciled by a model that includes the many degrees of thermodynamic freedom established by the multiplicity of pore radii in the porous medium.

Experimental Methods

The experimental methods used to form methane hydrate (using methane with minimum purity of 99.97 mol % obtained from Matheson) and to measure the equilibrium temperatures and pressures in a high-pressure cell during its subsequent dissociation are the same as those reported elsewhere.^{3,5} The pressure measurements were made with a 20.78 MPa full-scale transducer (Setra 204E transducer and Setra Datum 2000 reader) calibrated by the dead-weight method. The accuracy of the transducer was $\pm 0.1\%$ of full scale. Prior to the beginning of the decomposition experiments, excess gas left over from the hydrate formation process is present in the cell. To obtain the equilibrium pressure at the initial temperature, the gas pressure is reduced below the expected equilibrium pressure, and a small amount of hydrate dissociates until equilibrium is reached. The

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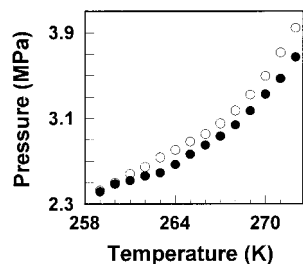


Figure 1. Experimental equilibrium pressures for methane hydrate formation in silica gels with a 5 nm nominal pore radius with percent conversions of pore-water to hydrate of 65% (●) and 96% (○).

temperature is then increased, sequentially, and the pressure recorded after equilibrium is reached at each temperature.

Results and Discussion

Henry et al.⁶ and Clark et al.⁷ presented modified van der Waals and Platteeuw⁸ equations to model hydrate formation in cylindrical pores. In the treatment of Henry et al.,⁶ the additional term, due to the capillary pressure, is proportional to the surface tension between the hydrate and water phases, and to the reciprocal of the pore radius. Instead of using the radius r and temperature T to predict the equilibrium pressure P , one can use the experimental T and P to determine the effective radius involved in each equilibrium. As a basis for a conceptual model for hydrate decomposition in porous media, consider a distribution of tubes with radii $r_1 < r_2 < r_3 \dots$, completely filled with hydrate. As the temperature rises, the pressure in the headspace will not be sufficient for all of the hydrate to remain stable. Since hydrate in smaller radii tubes requires larger pressures to remain stable,^{1,3,5} that in the smallest tubes decomposes first, raising the pressure in the headspace. If the total volume of gas available from tubes of radius r_1 is more than sufficient to raise the pressure in the headspace to that necessary to stabilize hydrate in these tubes, equilibrium will be reestablished before they are all exhausted, and the observed pressure will be the same as if the medium were solely made up of these tubes. If tubes of radius r_1 do not contain enough gas to raise the pressure by the required amount, all of the hydrate in these tubes will decompose, and hydrate in the next size tubes will begin to decompose. If the total volume from these two tube sizes is more than sufficient to raise the pressure to the equilibrium value for this larger tube, then some of the hydrate in tubes with radius r_2 will remain undecomposed, and the experimentally observed pressure at this temperature will be that which would be observed if the medium were solely made up of tubes having radius r_2 . Thus, at each temperature the observed equilibrium pressure corresponds to a single-size tube, but the size of the tube varies as the temperature is raised. In addition, the size of the tube involved in the equilibrium at a specific temperature depends on the relative sizes of the headspace and the amount of hydrate present in the sample, making the measured pressure appear to be an extensive property.

Figure 1 shows hydrate decomposition data for two experiments in pores of nominal 5.0 nm silica gel where the only difference between experiments was the percent conversion of water to hydrate (96% and 65%, respectively). A method to calculate hydration numbers,¹⁰ in conjunction with a hydration number reported in the literature,³ was used to calculate these percent conversions. From the headspace volume and the total amount of methane generated during the decompositions, the ratios of the headspace volume to the numbers of moles of methane sequestered as hydrate prior to any decomposition were

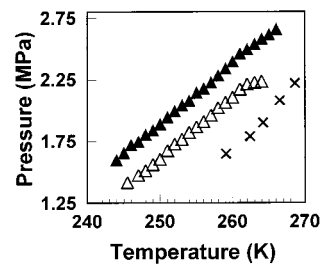


Figure 2. Experimental equilibrium pressures for methane hydrate formation in silica gels with a 2 nm nominal pore radius for samples SG2a (▲) and SG2b (△). Also shown are results for bulk hydrate formation¹¹ (×).

calculated to be 0.69 L/mol and 1.09 L/mol in the samples with 96% and 65% conversion, respectively. In these experiments, only a small amount of hydrate was allowed to dissociate prior to the first measurement, at 259 K (Figure 1), where both samples had equivalent equilibrium pressures. In each sample there was sufficient hydrate in the smallest pores to return the cell to equilibrium, leading to nearly identical equilibria. As the temperature was increased, the difference in the amount of hydrate in each size pore (due to the different percent conversions of water to hydrate) resulted in increasingly different sized pores being involved in the equilibria. This difference caused an increasing difference in the observed equilibrium pressures. While the hydrate sample with the lower percent conversion was completely exhausted at 275 K, the other was not exhausted until approximately 280 K, where the observed pressure was over 5 MPa. This pair of experiments, where the only difference was the percent conversion of water to hydrate, demonstrates the interaction of the headspace-to-hydrate ratio with the pore-volume distribution. In such data, the increase in equilibrium pressure as the temperature increases is actually the net result of two competing trends: a pressure increase due to the rise in temperature, and a decrease due to an increase in the radius of the pores that are at equilibrium at each higher temperature. The model proposed in this work suggests that a sample containing a narrow distribution of pore sizes would show a greater relative change in the equilibrium pressure with temperature, due to a lessening of the latter effect.

Data for a pair of experiments with nominal 2 nm pores are shown in Figure 2, where the percent conversions of water to hydrate were 27.6% (sample SG2a), and 47.1% (sample SG2b). The headspace-to-hydrate ratios were 2.55 L/mol and 1.77 L/mol, respectively. In these experiments the pressure in the cell was bled down well below the equilibrium pressure before the first pressure-temperature measurement, causing appreciable hydrate to dissociate before the initial equilibrium was established. Due to the lower percent conversion of water to hydrate in sample SG2a, more of its smaller-sized pores were exhausted during the re-pressurization by dissociation, and hence the initial equilibrium involved a larger pore size (leading to a smaller equilibrium pressure). The resulting difference in equilibrium pressures can be seen at the lowest temperatures in Figure 2. Calculations show that the small but significant difference between the effective pore radii for the two samples at the lowest temperatures increases to over 18% at 264 K, due to the smaller amount of hydrate present in each size pore in sample SG2a. This difference necessitates hydrate in larger and larger pores to dissociate in SG2a in order to reach equilibrium (leading to lower equilibrium pressures relative to SG2b). The change in behavior at the lowest temperatures between the two 5 nm and two 2 nm samples demonstrates how the amount of hydrate

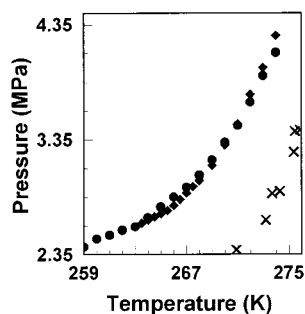


Figure 3. Experimentally measured equilibrium pressures in silica gels of nominal pore radii 5 (●) and 7.5 (◆) nm. Also shown are results for bulk hydrate formation¹¹ (×).

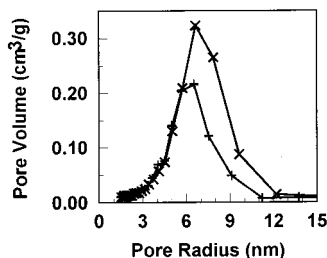


Figure 4. Pore volumes based on the Autosorb-1 desorption data in Figure 1 for silica gels with nominal 7.5 nm (×) and 5.0 nm (+) pore radii.

allowed to dissociate prior to an equilibrium measurement affects the observed pressure.

Figure 3 shows equilibrium pressures for media with pores of nominal 7.5 and 5.0 nm radii. A casual inspection of the data suggests (incorrectly) that pore size has little effect on the equilibrium pressures. More careful inspection shows that the correct conclusion is the following: *The nominal pore size of a sample cannot be used to interpret hydrate equilibrium data in porous media.* Figure 4 shows the pore-volume distributions of these two media calculated¹² from nitrogen adsorption data. As can be seen, the two are identical up to a pore radius of about 6 nm. Equilibria in pores up to this size led to the close correspondence in the equilibrium pressures shown in Figure 3 up to a temperature of 271 K, at which temperature calculations show that the equilibria in both experiments involved pores with radii approximately equal to 6.1 nm. As seen in Figure 3, the data for the two samples appear to diverge after this point. This divergence is due to the increasing differences in the pore-volume distributions beyond 6.1 nm shown in Figure 4. The divergence demonstrates the effect of different pore-volume distributions on the observed equilibrium pressure. Above 271 K, the hydrate in pores where the two distributions coincide has all been exhausted, and in the nominal 5 nm sample hydrate in larger sized pores must be exhausted to reestablish equilibrium at each successive temperature, leading to lower equilibrium pressures.

The small differences in Figure 3 between the equilibrium pressures between 264 and 270 K can also be explained. Though there was a larger percent conversion in the 7.5 nm sample (84% vs 65% for the nominal 5 nm silica gel), the 5 nm silica gel actually contained 16% more hydrate (due to a larger silica gel sample size), and had a 13% smaller headspace volume (also due to the larger sample size), leading to a higher headspace-to-hydrate ratio. Therefore, the 5 nm sample had more hydrate in each size pore (due to the larger total sample size). This led

to a slightly smaller size pore being involved in the equilibrium at each temperature, and thus slightly higher pressures. The equivalence of the equilibrium pressures at 264 K demonstrates the effect of initial temperature on the equilibrium pressure observed at subsequent temperatures. Though in both experiments the cell was bled to approximately the same pressure before the first equilibrium measurement, the experiments in the 5 nm silica gel started 4.5 K below the initial temperature for the 7.5 nm sample. The additional hydrate decomposed at these lower temperatures in the 5 nm sample compensated for the higher total amount of hydrate present in the involved pores, resulting in equivalent equilibria near 264 K.

The data for nominal 7.5 nm silica gel pores coincide with data in the literature³ for this nominal pore size at the lowest temperatures, and diverge moderately as the temperature increases (similar to Figure 1). The percent conversion of water to hydrate in our 7.5 nm sample was only 84% (relative to that of Handa and Stupin³). While this could explain the differences (see the discussion of Figure 1 above), a quantitative comparison of the headspace-to-hydrate ratios cannot be made due to the absence of needed data for the previously published experiments.

Summary

Observed hydrate equilibrium pressures in porous media that have broad pore-size distributions depend on the interaction of four factors: (1) the headspace-to hydrate ratio after hydrate formation; (2) the temperature at which the first equilibrium measurement is made; (3) the amount of hydrate allowed to dissociate to establish equilibrium at this initial temperature; and (4) the pore-volume distribution of the porous medium. The complex interaction of these factors can lead to erroneous conclusions when one attempts to interpret observed equilibrium pressures in porous media without proper treatment of the many degrees of thermodynamic freedom established by the multiple pore radii. The consideration of these factors is essential for correct comparison/explanation of experimental results for hydrates in porous media that contain broad pore-size distributions of small pores and identical media.

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References and Notes

- (1) Makogon, Y. F. *Hydrates of Natural Gas*; PennWell: Tulsa, 1981.
- (2) Kamath, V. A. University of Pittsburgh, Ph.D. Dissertation, 1984, University Microfilms No. 8417404.
- (3) Handa, Y. P.; Stupin, D. J. *Phys. Chem.* **1992**, *96*, 8599.
- (4) Uchida, T.; Ebinuma, T.; Ishizaki, T. *Phys. Chem.* **1999**, *103*, 3659.
- (5) Seshadri, K.; Wilder, J. W.; Smith, D. H. *J. Phys. Chem. B* **2001**, *105*, 2627.
- (6) Henry, P.; Thomas, M.; Clennell, M. B. *J. Geophys. Res.* **1999**, *104*, 23005.
- (7) Clarke, M. A.; Pooladi-Darvish, M.; Bishnoi, P. R. *Ind. Eng. Chem. Res.* **1999**, *38*, 2485.
- (8) van der Waals, J. H.; Platteeuw, J. C. *Adv. Chem. Phys.* **1959**, *2*, 1.
- (9) Handa, Y. P.; Zakrzewski, M.; Fairbridge, C. J. *Phys. Chem.* **1992**, *96*, 8594.
- (10) Handa, Y. P. *J. Chem. Thermodyn.* **1986**, *18*, 891.
- (11) Sloan, E. D. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker: New York, 1997.
- (12) Lowell, S.; Shields, J. E. *Powder Surface Area and Porosity*; Chapman and Hall, New York, 1991; pp 52–71.